SILVER SODALITES

NOVEL OPTICALLY RESPONSIVE NANOCOMPOSITES

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ABSTRACT

A range of novel silver sodalites have been synthesized. These solid state microstructures are viewed as "packaged" silver salts comprised of nanoassemblies of silver cations tetrahedrally organized with various charge balancing anions. A collection of physicochemical characterization techniques (UV-VIS reflectance/emission/excitation; luminescence lifetimes; FT-FAR/MID-IR; XPS; TGA-MS; ^{29}Si, ^{27}Al, ^{23}Na MAS-NMR; Rietveld XRD profile analysis) have been employed to interrogate the structure and properties of the parent silver sodalites, as well as the chemical and physical transformations of the encapsulated silver salts that relate to a number of interesting transducer effects. Intercavity communication between entrapped silver microaggregates and expanded-metal superlattice ideas will be considered briefly. The utilization of the silver sodalites in high resolution imaging/printing and high density write/read/erase data storage applications are also considered.

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INTRODUCTION

The myriad of one, two and three dimensional, molecular size channel and cage structures found in the class of crystalline framework materials referred to as zeolites, confers upon them a unique spatial quality displayed by few other classes of solid state materials. With this in mind, recall that today's world of advanced solid state materials is unrelentingly driven by the ever increasing demands for smaller, faster, more selective and efficient products and processes. Thus one can justifiably ask whether or not the well known structural, physical and chemical properties of zeolites together with their size and shape discrimination power, traditionally applied in catalysis, selective adsorption, molecular sieving, water softening and waste water clean-up to name a few, can be effectively exploited in emerging new fields of solid state chemistry.

One of the points that will emerge from this paper, as well as others to be presented at this conference, is that microporous molecular electronic materials with nanometer dimension window, channel and cavity architecture represent a "New Frontier" of solid state chemistry with great opportunities for innovative research and development.

SILVER SODALITES: NOVEL, OPTICALLY RESPONSIVE, PACKAGED SILVER SALTS

A range of novel silver sodalites have recently been synthesized[1]. These solid state microstructures are viewed as "packaged" silver salts comprised of nanoassemblies of silver cations tetrahedrally organized with various charge balancing anions[2]. A collection of physicochemical characterization techniques have been employed to interrogate the structure
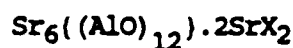
and properties of the parent silver sodalites, as well as the chemical and physical transformations of the encapsulated silver salts that relate to a number of transducer effects[3]. An interesting question in these materials concerns intercavity communication between aggregates of the entrapped silver salt and the connection of their properties with those of the analogous bulk phase material (such as electronic transport, photoconductivity, photoaggregation and photoluminescence). Intracavity redox processes that produce encapsulated silver clusters and expanded-metal-superlattice phenomena above the percolation threshold loading level are also intriguing avenues of enquiry within the silver sodalite family of materials.

In this summary paper we will briefly explore the synthesis and characterization of a *few key* silver sodalites and examine their possible utilization in high resolution imaging/printing and high density data storage applications.
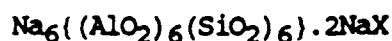
A summary of some of the attractive features of silver sodalites in solid state chemistry is presented schematically in Figure 1. The regular, all space filling, cubic framework of sodalite (a Federov solid) provides a homogeneous microporous matrix of 6.6 Å sodalite cavities, suitable for stabilizing small isolated molecules, atoms and clusters as neutral species, ions or even radicals[2] (Figure 2). The unit cell dimensions, charge balance requirements and cage-filling can all be tuned by incorporating a large variety of anions during the sodalite synthesis. Various sodalite cage anion packing schemes are illustrated in Figure 3. Variation in the Si/Al ratio from pure aluminate to pure silica sodalite are also possible as summarized in Scheme 1.

SCHEME 1
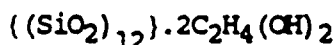
PURE ALUMINATE SODALITE (Si/Al = 0)[6]	$Sr_6((AlO)_{12}) \cdot 2SrX_2$
NORMAL SODALITE AT THE LOEWENSTEIN LIMIT (Si/Al = 1)[2]	$Na_6((AlO_2)_6(SiO_2)_6) \cdot 2NaX$
SILICA-RICH TMA SODALITE (Si/Al = 5)[7]	$(CH_3)_4NAlSi_5O^{12}$
POROUS, CRYSTALLINE SILICA SODALITE (Si/Al = ∞)[8]	$((SiO_2)_{12}) \cdot 2C_2H_4(OH)_2$

This impressive range of sodalite cage compositions attests to the remarkable isomorphous replacement qualities of the sodalite framework topology[2]. Substitution of the framework atoms (Si^{4+}, Al^{3+}) for other elements, such as, Ge^{4+}, Ga^{3+}, B^{3+}, P^{5+}, Fe^{3+} allows further control over the material properties. Sodalites with sodium cation guests are readily synthesized by hydrothermal reactions of silicate and aluminate sources (e.g. kaolin; or silica gel and sodium aluminate) with the appropriate anion salt in concentrated NaOH solutions[2,3].

Sodium ions are exchanged by silver ions in a silver salt melt, or in some instances, in a silver salt aqueous solution. The framework structure is generally maintained after exchange, as confirmed by powder X-ray diffraction and mid-IR of the framework vibrations[3]. The silver sodalites prepared to date in our laboratory are listed in Table 1. The silver exchange process is conveniently monitored by intensity changes of

diagnostic sodium and silver ion translatory modes in the far-IR as well as shifts in the frequencies of far-IR anion translations[9] (Figures 4,5).

Many of the silver sodalites prepared in our studies are novel materials. Interesting responses in color as well as luminescence properties are observed upon exposing several compositions to a variety of physical stimuli, including heat, light, pressure, moisture, X-rays and e-beams. These effects are categorized in Table 2. Some of these changes were reversible or semi-reversible[1], the details of which will be published elsewhere.

These effects are related to the ease of silver reduction and the ability of the silver to form small clusters or expanded superclusters within the sodalite framework. In silver hydroxo-, formato- and oxalato-sodalites this is facilitated by intrazeolitic redox reactions:

$$2\ Ag^+(Z) + H_2O(Z) \longrightarrow 2\ Ag^0(Z) + 1/2\ O_2 + 2\ H^+(Z) \qquad [1]$$

$$2\ Ag^+(Z) + OH^-(Z) \longrightarrow 2\ Ag^0(Z) + 1/2\ O_2 + H^+(Z) \qquad [2]$$

$$2\ Ag^+(Z) + HCO_2^-(Z) \longrightarrow 2\ Ag^0(Z) + CO_2(Z) + H^+(Z) \qquad [3]$$

$$2\ Ag^+(Z) + C_2O_4^{2-}(Z) \longrightarrow 2\ Ag^0(Z) + 2\ CO_2 \qquad [4]$$

Reaction [4] can be effected both thermally and photolytically. Note that these equations are intended to illustrate simple stoichiometric redox reactions and are not meant to represent balanced unit cell reactions. Depending on the level of silver exchange, aggregates of the type $(Ag_nNa_{4-n})^{q+}$, n = 0 to 4, may be formed within the cages, where charge variations of q in the range q = (4-n) to 4 can lead to the observed optical responses.

By increasing the silver loading in the parent sodalite, it is possible to form cluster and extended supercluster structures in the quantum size regime. Such superclusters have been reported in the case of semiconductor materials in faujasites and zeolite A.[10] One important advantage of sodalites over the other zeolite hosts is that the sodalite lattice is not comprised of coexisting sodalite and supercages but is instead entirely composed of close-packed sodalite cages, thereby permitting direct or through-bond interaction between silver guests in all cages. In addition, sodalites are unique due to the presence of guest-anions, which can not only be used as internal reagents (e.g. for intra-sodalite cage redox reactions) but also provide great flexibility in the composition of trapped species. By judicious selection of the anion and cation one can form packaged insulators, semiconductors as well as metals within the sodalite framework. Control of the guest-concentration in sodalites allows transitions from molecular type species to expanded bulk materials above a percolation threshold (PT), as illustrated in the following scheme:

SCHEME 2
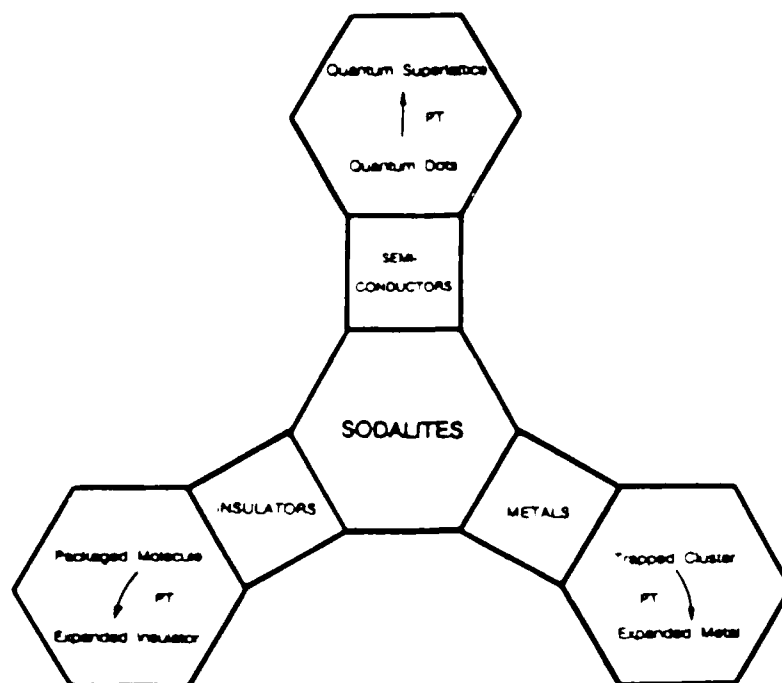
The oxalato system has been studied in greatest detail with various silver loadings. The results of a full-profile Rietveld analysis[11] of X-ray powder diffraction data for completely silver ion-exchanged Ag,Ox-SOD are illustrated in Figure 6. The data were refined, allowing for three types of silver, each statistically distributed. A good refinement was obtained which is reflected in the small value of x^2 = 2.16 and final R factors of wR_p = 0.140, R_p = 0.107. In accordance with the -2 charge on the oxalate anion, both anion filled Ag_4Ox and empty Ag_4 cages are observed displaying a tetrahedral disposition of Ag atoms with each Ag coordinated to three oxygen atoms in adjacent six-rings. The intracage Ag-Ag distance is ca. 6 Å for oxalate ion-containing cages and 5.5 Å for empty Ag_4 cages, with intercage Ag-Ag distances of 4.5 Å and 4.6 Å, respectively. For those cages exhibiting some loss of AgOH (extracted in a hot washing procedure) residual Ag_3 triangles are observed with an intracage Ag-Ag distances of 4.5 Å and an intercage Ag-Ag distance of 4.9 Å.[11] These interatomic distances are too long for direct overlap of the silver orbitals but they are well within the range of through-bond interaction involving the sodalite framework. Such long range interactions would allow the formation of an expanded silver supercluster, similar to a recently reported $(CdS)_4$ supercluster formed in the sodalite cages of zeolite Y above the percolation threshold, with Cd to Cd distances of ca. 6 Å between adjacent sodalite cages.[10]

After aqueous silver exchange, sodium/silver oxalato-sodalites are white. Following thermal treatment at a temperature allowing for oxalate decomposition, the materials absorb light in the UV and visible regions, the absorption spectrum depending on the silver concentration (Figure 7). Concentration effects are also exhibited by the position of the most intense

emission bands[3]. Variations in both the identities of trapped silver clusters and the unit cell sizes can be responsible for the shifts in transition energies.

It is important to note that in the virgin Na,Ag,Ox-SOD samples, one does not observe a linear increase of the unit cell dimension with Ag^+ loading (Figure 8). The largest increase in unit cell size occurs following the introduction of what appears to be less than a single Ag^+ per unit cell. One deduces therefore that the observed changes in unit cell size are not "purely" $R(Na^+)$ and $R(Ag^+)$ spatial effects but instead contain subtle contributions arising from electronic, bonding and coordination differences between Na^+ and Ag^+ cations.

Another point that emerges from the XRD data for Na,Ag,Ox-SOD as a function of Ag^+ unit cell content, concerns the question of the distribution of silver in sodalites with mixed Na^+/Ag^+ compositions. Three models require serious consideration:

a)   domains of $4Na^+$ and $4Ag^+$

b)   ordered $(Na^+)_n(Ag^+)_{4-n}$ (n fixed)

c)   statistical $(Na^+)_n(Ag^+)_{4-n}$ (n = 0 - 4).

From the XRD results, one can eliminate ordered model (b) as no superlattice reflections were observed. Also no splitting or broadening of XRD lines expected for a domain model (a) were noticed after silver addition. Furthermore, a_0 does not appear to change abruptly with Ag^+ loading, indicative of an alteration from one ordered phase to another. On these grounds one can conclude that the observed smooth, monotonic change in a_0 with Ag^+ in Na,Ag,Ox-SOD implies the statistical model (c) and the existence of a "solid solution" of β-cage encapsulated $(Na^+)_n(Ag^+)_{4-n}$

moieties.

In this context the silver concentration dependence of ^{23}Na MAS-NMR chemical shifts is particularly interesting[11]. To begin with, ^{29}Si and ^{27}Al MAS-NMR data for the parent Na,Ox-SOD shows evidence of three types of sodalite cage, that is, Si(4Al) and Al(4Si) tetrahedral groupings corresponding to distinct β-cage contents, namely $\beta(C_2O_4^{2-})$, $\beta(OH^-)$ and β(empty), cf. Figure 6. Also one knows that the ^{29}Si chemical shift for a large range of sodalites directly correlates with the unit cell dimension a_0 and the SiOAl angle α.[12] Here ^{29}Si shielding increases with α, paralleling enhanced O(pπ) —> Si(dπ) charge-transfer. We find a smooth correlation of the ^{23}Na chemical shift with a_0 as the Ag$^+$ content of the unit cell is increased (Figure 8). As one knows that a_0 and α are linearly dependent, one can deduce that the observed monotonic trend in ^{23}Na chemical shifts for Na,Ag,Ox-SOD with increasing Ag$^+$ content originates from a sympathetic change in α, mainly traceable to alterations in the Lamb diamagnetic contribution to the ^{23}Na chemical shift. This arises from a constant decrease in charge density from the sodalite cage lattice six-ring oxygens to Na$^+$(3s) as that to Si increases. On a final note, the ^{23}Na MAS-NMR chemical shifts described above refer to average values for the different distributions of Na$^+$ cations, in three distinct β-cages for the hydrated Na,Ag,Ox-SOD materials as a function of Ag$^+$ loading. Hydration levels and quadrupole broadening/relaxation effects have yet to be evaluated.

The fate of the oxalate ion during thermal treatment was followed by thermogravimetric analysis coupled with mass spectrometry (TGA-MS)[3], mid-IR spectroscopy[3] and powder X-ray diffraction[11], Figure 9. Comparison of the results for sodium oxalato-sodalite and silver oxalato-sodalite indicates

that the reduction potential of the cation directs the reaction mechanism. While in the silver oxalate sodalite the anion is oxidized to CO_2 with concomitant reduction of the silver ions, oxalate ion decomposition in the sodium oxalate sodalite produces CO and CO_3^{2-}, with no redox reaction occurring[3]. In mixed sodium/silver oxalato sodalites the degree of silver exchange can thus be used to control not only the optical and structural properties, but also the thermal behaviour of the sodalite.

The question of the extent of silver reduction following thermal decomposition of Ag,Ox-SOD has been addressed from the TGA-MS analysis of CO_2 and O_2 evolution[3]. This provides an "ideal case" estimate of the maximum degree of silver reduction. With reducing electron equivalents derived from intra-β-cage $C_2O_4^{2-}$ decomposition (Equation [4]) and autoreduction by intra-β-cage water and hydroxide (Equations [1] and [2]) one calculates that the maximum change in oxidation state of silver amounts to an average of only $0.5e^-$ per unit cell, corresponding to 6% per silver ion. This nicely accounts for our XPS analysis[3] of the parent and thermally decomposed Ag,Ox-SOD which shows very little change in the silver ion core level ionization energies.

In concert with the TGA-MS data it is intriguing to note the corresponding alterations in unit cell dimension a_0 in Ag,Ox-SOD and its parent Na,Ox-SOD with temperature[11] (Figure 9). In both cases a drastic cell expansion occurs as water is driven out of the sodalite cages paralleling the results reported for Na_6-SOD·$4H_2O$ $\longrightarrow$ Na_6-SOD.[13] This unusual phenomenon is ascribed to the loss of structural hydrogen-bonding between the encapsulated H_2O and the sodalite framework oxygens, thereby allowing the cage to "flex and expand". Of particular importance is the

measurable decrease in unit cell dimension of Ag,Ox-SOD and Na,Ox-SOD around 350°C and 450°C roughly corresponding to the thermal decomposition of $C_2O_4^{2-}$ to $2CO_2$ and CO/CO_3^{2-} respectively.[11] This is nicely in line with our TGA-MS observations which show the evolution of CO_2 or CO in these temperature regions.[3]

Although the number of electron equivalents involved in intracavity silver ion reduction is relatively small, the alterations in silver cluster optical properties that ensue are quite spectacular, (Figure 7). As a result, the silver sodalites lend themselves to applications in high resolution imaging and optical data storage[1], because the regular close-packed framework structure contains small entrance windows with 2.2 - 2.6 Å diameters and single-size cages with 6.6 Å diameters, which can trap and stabilize clusters formed inside. During a write cycle these clusters can be manipulated by the physical or chemical treatments described above (Table 2) to change their optical properties and produce a mark on the sodalite samples. The presence or absence of an optically absorbing or fluorescing mark defines a binary state. The size of the mark is affected mainly by the silver distribution, the sodalite particle size and the writing mechanism employed. The sodalite may be in the form of a self-supporting pressed disk, suspended in another material (e.g. glass or polymer), or supported on a substrate as a thin film[1].

Further research efforts will be directed at characterizing the silver clusters responsible for the optical properties of silver sodalites, and at fine-tuning the compositions of these compounds to optimize their responses.

CONCLUSION

Assembling the information from the present study of silver sodalites one can deduce that:

i) silver sodalites can be synthesized with a variety of optochromic responses;

ii) the distribution of β-cage encapsulated $(Na^+)_n(Ag^+)_{4-n}$ moieties is statistical (solid-solution like as a function of n);

iii) framework destruction occurs under strongly reducing (e.g. H_2 at 350°C) conditions;

iv) the properties of the sodalites can be controlled by the nature of the anion and cation and their relative concentrations.

Specifically, the optochromic responses in the silver sodalites are determined by:

v) the ease of silver reduction;

vi) the ease of anion decomposition if a redox reaction is involved.

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FIGURE CAPTIONS

1. Summary of features of silver sodalites of interest in solid state Chemistry.

2. A) Sodalite cage of SiO_4^{4-} and AlO_4^{5-} tetrahedra showing the oxygen bridges.[4] B) Unit cell of sodalite with [Na_4Cl] tetrahedra at the centre and corners of the cell.[4] C) Stereoplot showing the close packing of cages in the sodalite structure.[5]

3. The effect of charge restrictions in a 1:1 aluminosilicate sodalite with monovalent cations. An idealized layer of sodalite cages is shown in each case. Extraframework cations are left out for clarity. A) Each cage is occupied by a monovalent anion. B) A trapped electron (F-centre) can replace an anion in photochromic or cathodochromic sodalites. C) Divalent anions require that half of the cages do not contain negative ions. D) Anion mixing allows some control over negative ion deficiencies in the sodalite cages.

4. Far-IR spectra of chloro-sodalites with various silver loadings. A) Na,Cl-SOD. B) Na,Ag,Cl-SOD (1 Ag/u.c.). C) Na,Ag,Cl-SOD (2 Ag/u.c.). D) Ag,Cl-SOD (8 Ag/u.c.). The spectra are not all shown on the same absorbance scale. "f" denotes a framework absorption.

5. Far-IR spectra of halo-sodalites, A) Ag,Cl-SOD. B) Ag,Br-SOD. C) Ag,I-SOD. D) Na,Cl-SOD. E) Na,Br-SOD. F) Na,I-SOD. "f" denotes a framework absorption.

6. Four cages of Ag,Ox-SOD showing the framework of SiO_4^{4-} and AlO_4^{5-} units, silver ions, the oxalate anion, and water molecules. Except for hydrogen atoms and the oxalate ion, all atoms were located by a Rietveld profile analysis of powder x-ray diffraction data (wR_p = 0.140, R_p = 0.107).[11]

7. UV-visible reflectance spectra of oxalato sodalites. A) Na,Ox-SOD (white). B) Na,Ag,Ox-SOD (1 Ag/unit cell), (light grey). C) Na,Ag,Ox-SOD (2 Ag/unit cell), (bluish grey). D) Ag,Ox-SOD (green). E) Ag,Ox-SOD, exposed to sunlight for four days (pale yellowish green). Samples B - E were prepared by melt exchanges.

8. Variation in the unit cell sizes of Na,Ag,Ox-SOD and ^{23}Na MAS-NMR chemical shifts as a function of silver loading.

9. Variation in the unit cell sizes of Na,Ox-SOD and Ag,Ox-SOD with temperature. A drastic cell expansion occurs as water is lost. When the sodalites release CO or CO_2, respectively, the unit cell size decreases slightly.

Silver sodalites prepared in this study.

Sodalite Type	Reason for Study
Ag,Cl-SOD Ag,Br-SOD Ag,I-SOD	Analogues to photochromic and cathodochromic sodalites; Similarities with photographic process; Occluded guest species are photo-conductors, semiconductors, fast-ion conductors; Study variation in properties down a group.
Ag,S-SOD[a] Ag,Br,S-SOD	Sensitization; Photographic Imaging.
Ag,OH-SOD	Some hydroxide present in most hydrothermally prepared sodalites.
Ag_6-SOD	Cages contain only three silver ions and no anion; Occluded metal clusters; Expanded metal; Quantum size effects.
Ag,CO_3-SOD Ag,HCO_2-SOD = Ag,Fo-SOD Ag,C_2O_4-SOD = Ag,Ox-SOD Ag,ClO_4-SOD Ag,SO_x-SOD	Intracage anion decomposition possible; Redox switching.
Na,Ag,X-SOD	Mixed cation systems to study silver concentration effects; Tunable insulators/semiconductors (NaX: insulators; AgX: semi-conductors, ion conductors).

Notes: a)   An XRD powder diffraction analysis indicated that significant framework decomposition occurred during the synthesis of Ag,S-SOD by melt exchange.

Qualitative responses of silver sodalites to various physical stimuli.

BAROCHROMIC:

White Ag,OH-SOD or Ag,HCO$_2$-SOD samples darken upon application of pressure.

HYDROCHROMIC:

Ag,OH-SOD undergoes a reversible color change upon dehydration.

PHOTOCHROMIC:

Color changes and/or sample darkening can be produced by irradiation of Ag,Ox-SOD, Ag,OH-SOD, AgCO$_3$-SOD, Ag,HCO$_2$-SOD and sulfur-doped silver sodalites with various light sources.

THERMOCHROMIC:

Na,Ag,Ox-SOD, Ag,OH-SOD and sulfur-doped silver sodalites undergo various color changes upon heat treatment.

X-RAY SENSITIVITY:

White Ag,Ox-SOD turns yellowish green upon exposure to x-rays.

FLUORESCENCE CHANGES:

Heat, light and x-rays can induce Na,Ag,Ox-SOD samples to fluoresce under UV-light.

Sodalite Framework as Stable Matrix for Trapped Clusters

Polytetrasilver Sodalite "Expanded Metal"

Silver Ions:

* Easily Reduced
* Easily Exchanged Into Sodalite
* Monitor Ion Exchange By Far-IR

Why Silver Sodalites?

Silver Clusters As Fluorescence Probes

Electronic and Ionic Conductivities

Photographic Process:

$$X^- + h\nu \longrightarrow X^0 + e^-$$
$$Ag^+ + e^- \longrightarrow Ag^0$$

Possible Applications as High Resolution Imaging and Optical Data Storage Materials

Precedents Of Various Silver Clusters In Other Zeolites

A   ● Si, Al   ○ o

B   ○ Na   ○ Cl

C

F3

C

D

A

B

S2- S2- S2-

Br- Br- S2- S2-

Cl- Cl- Cl- Cl- Cl- Cl-

Cl- Cl- Cl- e- Cl- Cl-

ABSORBANCE

WAVENUMBER (cm⁻¹)

ABSORBANCE

WAVENUMBER (cm⁻¹)

WAVENUMBER (cm⁻¹)
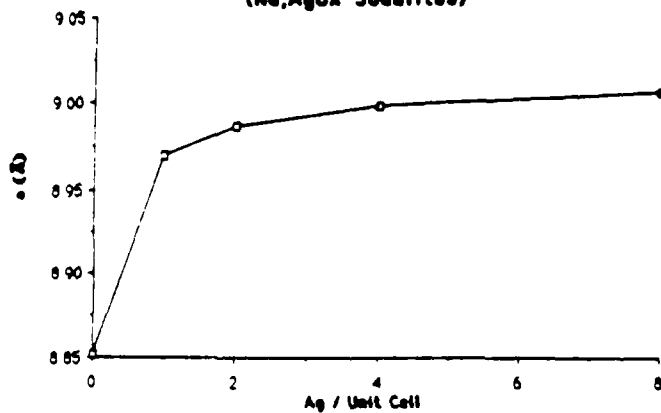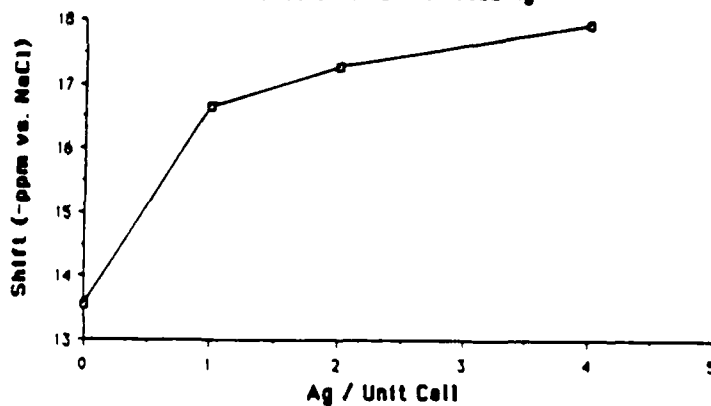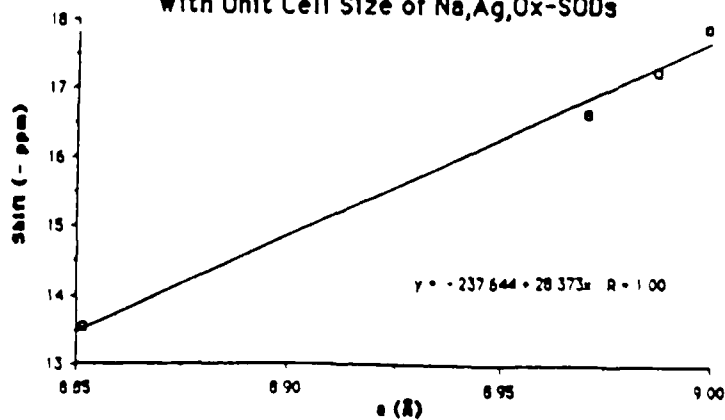
Variation of Unit Cell Size with Silver Concentration
(Na,AgOx-Sodalites)

Na-MAS Chemical Shift of Na,Ag,Ox-Sodalites·
As a Function of Silver Loading

Variation in Na-23 NMR Chemical Shift
With Unit Cell Size of Na,Ag,Ox-SODs

y = -237.644 + 28.373x   R = 1.00

Powder XRD Analysis

Figure: Powder XRD Analysis. Plot of a (Å) versus Temperature (°C), showing curves labeled Na,Ox-SOD and Ag,Ox-SOD.